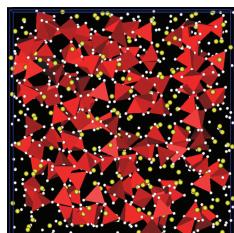


Savannah River/Hanford/Idaho Technical Exchange



Gene Daniel, SRNL
Sam Shah, LWO

TANK 48 FLUIDIZED BED
STEAM REFORMING
October 10, 2007

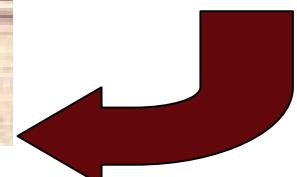


We Put Science To Work



THE PROBLEM A POTENTIAL SOLUTION

- T48 must be returned to service to support SWPF operation and free up SRS HLW tank space
 - Contains ITP legacy waste containing organic TPB
 - organic TPB must be destroyed / removed before returning to service
- Potential Solution: Fluidized Bed Steam Reforming to destroy organics TPB
 - Product can be returned to Tank Farm for further processing as HLW
 - Tank 48 can be returned to service



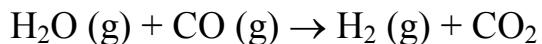
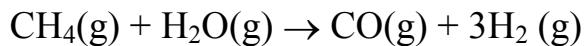
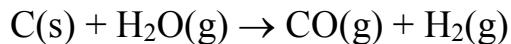
FLUIDIZED BED STEAM REFORMING (FBSR)

WHAT IS IT?

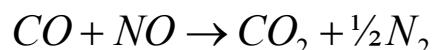
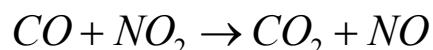
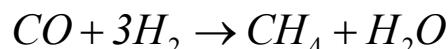
- FBSR is a moderate temperature robust technology
 - Operates at 625-750°C in the absence of air or oxygen
 - Reactions include organic destruction, denitration, evaporation, dehydration, and hydrothermal reactivity
 - Accommodates wide range of feeds
- Produces solid mineral phases from aqueous solutions
 - High Na containing wastes (NaOH, NaNO₃, NaNO₂, etc) can be made into sodium carbonates, sodium aluminates, sodium silicates, or Na-Al-Si (NAS) minerals
- FBSR non-radioactive Pilot Scale unit is available at SAIC / STAR facility at Idaho Falls and Engineering Scale unit at Hazen Research (Colorado)
 - Pilot scale demonstrations done with highly basic and acidic wastes
 - Engineering scale demonstrations done with SBW and T48 waste
- FBSR Bench-scale Steam Reformer (BSR) available at SRNL
 - BSR demonstrations done with highly basic and acidic simulated wastes (Hanford LAW, INL SBW)

FLUIDIZED BED STEAM REFORMING TYPICAL GAS REACTIONS

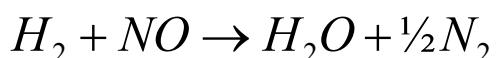
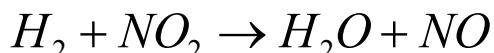
Water Gas Shift Reactions



Reactions that Convert CO to CO₂



Reactions that Convert NO₂ to N₂



- **Clean Air Act (CAA) compliant**
- **Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) compliant for Hg, CO, Cl, THC, heavy metals by pilot scale testing at INL^{1,2}**

PILOT SCALE SINGLE REFORMER FACILITIES

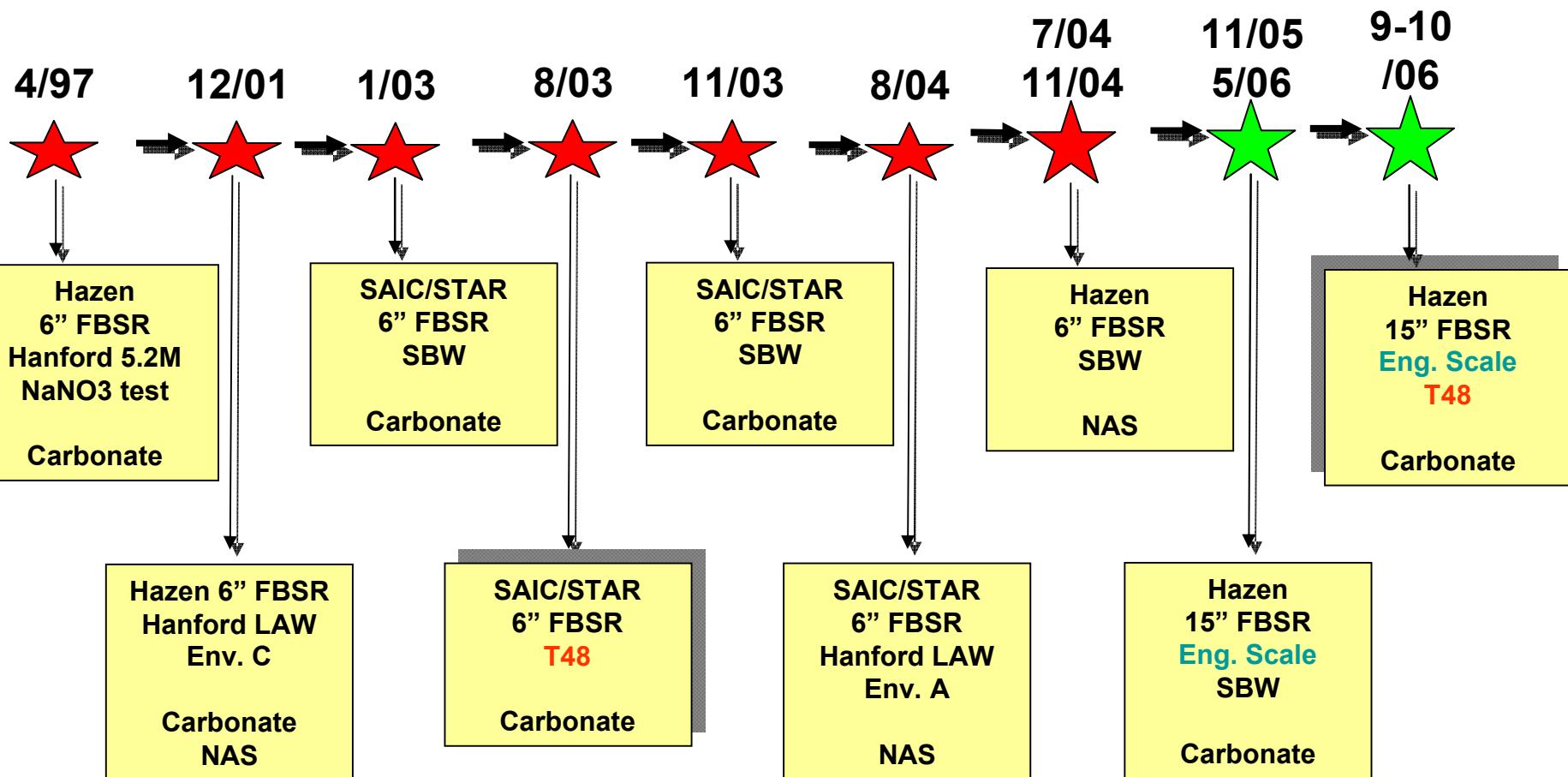


**INL SAIC STAR FACILITY
6" FBSR**

**HAZEN FACILITY
6" FBSR**



FBSR PILOT & ENGINEERING SCALE DEMONSTRATIONS



THOR® FLUIDIZED BED STEAM REFORMING COMMERCIAL OPERATIONS

- FBSR is a proven technology in the destruction of organics
 - Heavily shielded commercial operations destroy Cs¹³⁷ and Co⁶⁰ organic resins from nuclear power plants at Erwin, TN
 - Licensed as non-incineration technology by Region IV EPA to handle materials like ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions at radiation levels of up to 400R/hr
 - Organic destruction via pyrolysis



LAB SCALE STEAM REFORMING DEMONSTRATIONS

- Crucible Studies (2003-2005)
 - T 48 →NAS, carbonate product
 - SRNL & C Lab Waste (no Na, high Cl, F, NO₃, SO₄)
→ NAS, carbonate product
- BSR – 2" Fluidized Bed (FY04-05)
 - Hanford 5.0M Envelope A simulant → NAS product
 - Hanford 7.3M Envelope C simulant → NAS product
 - INL SBW simulant → NAS product
 - SRNL & C Lab Waste (no Na, high Cl, F, NO₃, SO₄)
→ NAS, carbonate product

LAB SCALE STEAM REFORMING RESULTS

- Optimized conditions defined for SAIC STAR pilot scale testing
 - bed material/product interactions
 - gas reactions (NO_x destroyed to >99%)
 - TPB destroyed >99.9% (from 95,100 ppm in simulant to <5 ppm in product)
- Tank 48 FBSR Carbonate products compatible with DWPF and Tank Farm
 - carbonate product can be processed in a single DWPF sludge batch

PILOT SCALE ORGANIC AND NITRATE DESTRUCTION COMPARABLE

- INL pilot unit operation using SRNL optimized conditions from sealed crucible tests was successful
 - FBSR destroyed TPB
 - NO_x destroyed to >99%
 - TOC destruction >99.5%
 - TOC < 1 wt %
- Optimized conditions from SRNL sealed crucible testing were duplicated in the INL pilot testing
 - product chemistry
 - bed material/product interactions
 - gas reactions (NO_x destroyed to >99%)
 - TPB destroyed >99.9%

THOR® PROCESS OVERVIEW

- **Waste feed tank(s)**
 - Receive waste, mix with additive (optional), inject into DMR
- **Denitration and Mineralization Reformer (DMR)**
 - Water is evaporated
 - Organics are oxidized or decomposed (e.g., to CO, CO₂, and CH₄)
 - Nitrates and nitrites are converted to nitrogen gas under reducing conditions
 - Waste constituents are converted into dry solid particles
- **Process Gas Filter (PGF)**
 - Remove fine waste particles from process gas
- **Carbon Reduction Reformer (CRR)**
 - NOx reduction, oxidize H₂, CO, VOCs to CO₂ and H₂O
- **Off-Gas system**
 - Cool off-gas, HEPA filtration, Hg removal, and discharge off-gas

THOR® PROCESS IMPLEMENTATION STATUS

Commercial nuclear experience

- **Studsvik Processing Facility (SPF), Erwin, TN**
 - Project design started: March 1997
 - Construction completed: Jan. 1999
 - Radioactive operations commenced: July 1999

DOE tank waste experience

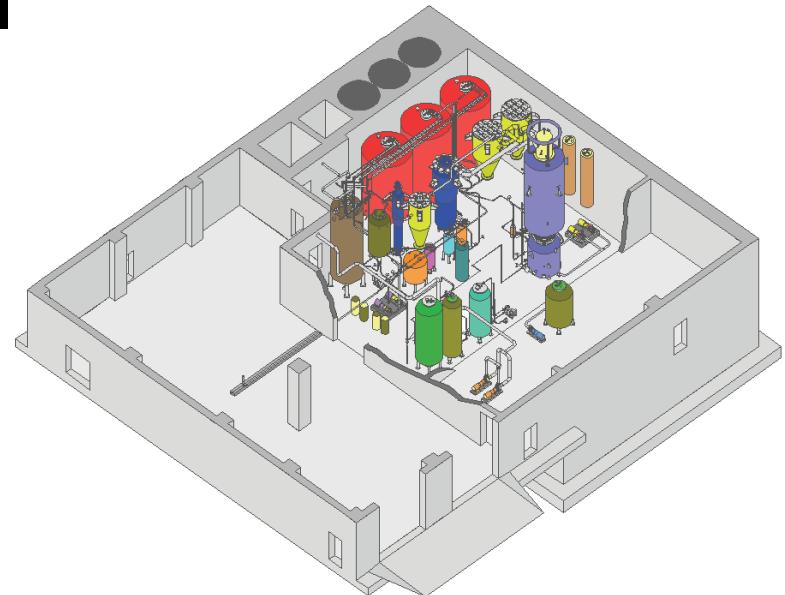
- **Idaho Cleanup Project – Integrated Waste Treatment Unit**
 - CD-0 (Justification of Mission Need) approved January 2005
 - CD-1 design started: March 2005
 - CD-1 (Preliminary Baseline Range) approved August 2005
 - CD-2 design approved by DOE: Dec. 2006
 - Construction commenced: April 2007
 - CD-3 design in progress; scheduled for submittal to DOE June 2007
 - Start SBW treatment by end of 2009
 - 15 months for treatment of ~1 million gallons SBW plus rinses

THOR® FBSR COMMERCIAL - SPF, ERWIN, TN

- **Full-scale facility treats commercial nuclear power plant waste**

- Radionuclide retention in solid products >99.9999% (2006)
 - Cs >99.999991%
 - Tc >99.99998%
 - Co >99.999995%
- >265,000 cu ft of LLW processed
- >2,360 incoming LLW shipments
- >92,000 Ci processed
- LLW dose rates up to 400 R/hr
- Over 7 years LLRW operation
- Waste feed: ion exchange resins, plastics, cellulose, carbon, oils: High salt content waste, High organic content

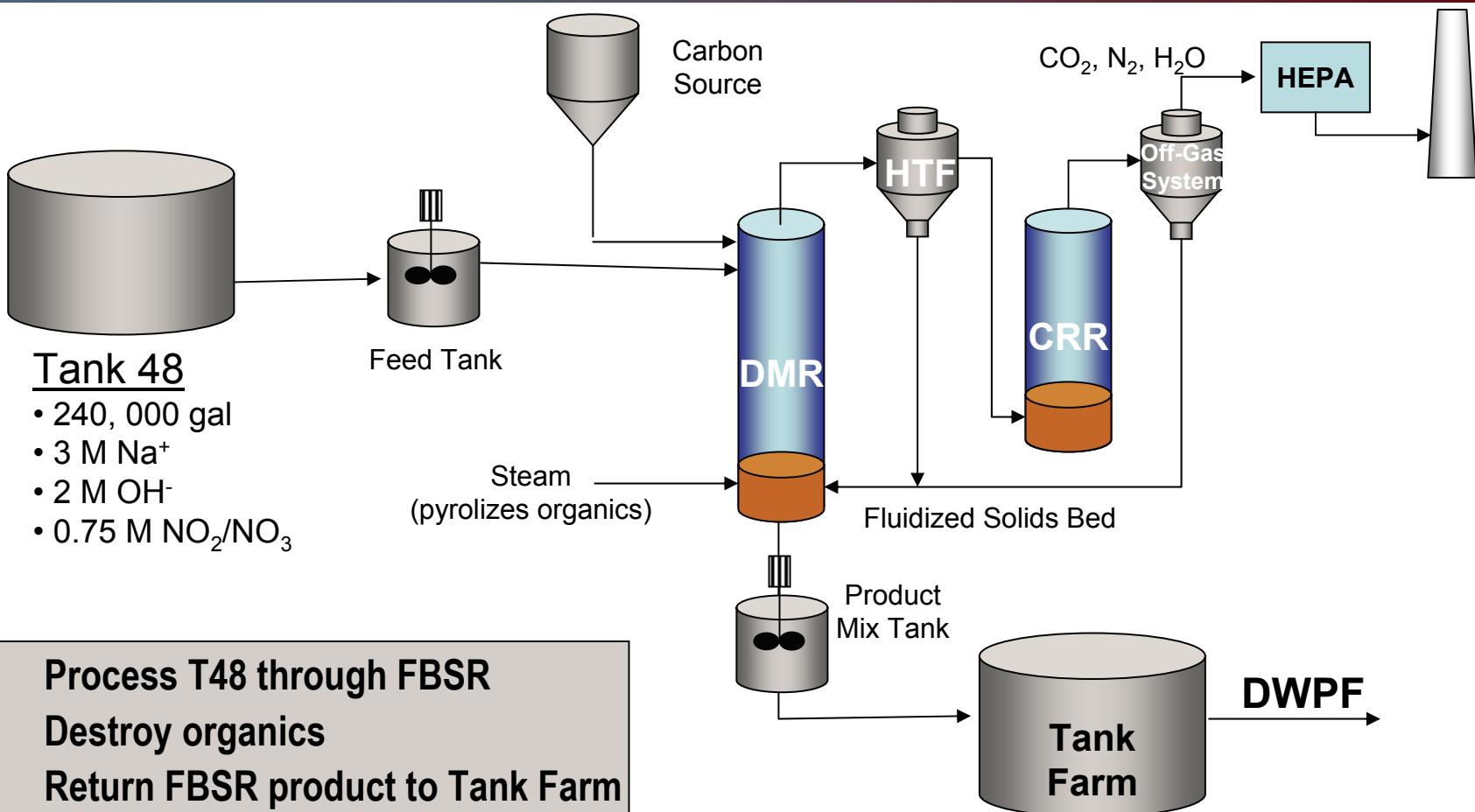
- **Developed mineralization additives**
- **2.5 years from design to LLW operations**



THOR® FBSR ENGINEERING SCALE TEST DEMONSTRATION

- To provide a high degree of confidence that the THOR® FBSR Process can successfully treat the Tank 48H waste on a production scale, the Engineering Scale Test Demonstration (ESTD) was operated using a Tank 48H waste simulant provided by WSRC
- The ESTD is a near full-scale integrated pilot plant that incorporates the key process unit operations for Tank 48H waste processing
- Experience has shown that this size equipment will accurately represent the production scale equipment in terms of:
 - Design
 - Operating parameters
 - Mass and Energy Balances

THOR® FBSR CONCEPTUAL FLOWSHEET FOR TANK 48



TANK 48H FBSR TEST PROGRAM OBJECTIVES

- Destroy > 99% of nitrates and nitrites to maximize conversion to nitrogen gas and minimize NOx emissions
- Destroy >99% of organics
- Capture F, Cl, Al, and other elements in solid product
- Remove >99% of Hg
- Generate no secondary liquid waste
- Gather emissions data for environmental permitting
- Generate solid product for analysis
- Demonstrate integrated system operation
- Demonstrate extended process operation
- Demonstrate acceptable material balance closure

OPTIMIZATION TEST OBJECTIVES

- Verify proper integrated system operation
- Confirm/establish basic system operating parameters for this flowsheet, e.g., DMR and CRR temperatures and DMR feed rate
- Evaluate alternate DMR reductants/energy sources and select best one for production test
- Optimize reductant usage to maximize nitrate destruction, minimize NOx generation, and minimize carbon in solid product
- Confirm operating parameters for overall system
- Choose energy source for CRR

OPTIMIZATION TEST RESULTS

- Optimization tests were conducted between 09/18/06 and 09/28/06
 - Tested various reductant/energy sources for the DMR
 - PE beads, PG, PE beads + PG, Sugar, Coal, Sugar + Coal
 - Only coal as DMR reductant produced acceptable results in terms of
 - In-bed energy production to sustain feed rate and bed temperature
 - In-bed residence time
 - No above-bed reaction
 - Process gas THC concentration
 - Acceptable operation of CRR without cooling water input
 - Tested PG as CRR fuel source
 - CRR operation with PG was superior to that with solid carbon for rapid response, ease of material handling and process operation
 - Off-gas species oxidation was as good as with solid carbon
 - Minimal solids carry over from CRR

OPTIMIZATION TEST RESULTS (CONT.)

- Tested DMR simulant feed rates 0.20 to 0.25 gpm
 - Both feed rates produced acceptable feed nozzle and DMR operation
- Operated DMR at 640 C and CRR at 950 C, typical for carbonate flowsheets
 - DMR and CRR operation were good at these temperatures, in conjunction with the other conditions noted above
 - Chose these temperatures to begin production tests
- Established other process parameters to begin production test, e.g.
 - DMR fluidizing gas velocity and air/steam flow rates
 - Feed nozzle atomizing gas ratio
 - CRR oxygen rates and nitrogen/oxygen ratios

PRODUCTION TEST RESULTS

- Integrated system operation was good
 - ✓ Verified DMR and CRR operating parameters
 - ✓ Confirmed coal as energy source/reductant for DMR
 - ✓ Demonstrated excellent performance of PG as CRR energy source
 - ✓ Confirmed performance of off-gas cooler and Hg absorber
- Demonstrated TPB Destruction Efficiency > 99%
- Process off-gas met MACT and other anticipated regulatory requirements and support permitting
 - POHC (MCB) destruction efficiency >99.99%
 - Stack THC <1 ppm
 - Hg removal efficiency >99%
- Produced good quality sodium carbonate-based product
 - Overall mass reduction was >70%
 - Volume reduction was ~52%
 - Feed nozzle performance was acceptable

ADDITIONAL TESTING RECOMMENDATIONS

- ❖ Test DMR Feed System under varying feed compositions
 - Feed Transport System from Feed Tank to DMR Nozzle
 - Feed Nozzle performance with <1 to 10 wt% solids
 - Process Response to varying feed conditions
- ❖ Test DMR fines / seed material control
 - DMR cyclone and downcomer performance (bridging / plugging)
 - Performance of HTF (filter plugging)
- ❖ Test reduction of large particle (coal) quantity in DMR product
 - Performance of dry / wet sieving mechanism
 - Recycling sieved material (> 200 mesh) back to DMR
 - Amount of small coal particles in DMR product to acceptable level

SUMMARY OF ENGINEERING SCALE TEST RESULTS

- ✓ **Demonstrated THOR® FBSR Process capability to destroy organics**
 - TPB Organic destruction > 99%
 - NO₃ destruction >99%
- ✓ **Demonstrated safe, predictable, integrated system operation**
- ✓ **Demonstrated off-gas compliance with regulatory limits**
- ✓ **Collected necessary data for Tank 48H process design, permitting, and operation**
- ✓ **Identified areas for future testing**

Future Testing

- **Pilot Scale FBSR Demonstration:**
 - Address prior testing recommendations and concerns
- **Crucible Scale FBSR Demonstration:**
 - Demonstrate Real Waste Tank 48 behaves like Tank 48 simulant in static FBSR-like chemical environment
- **Bench Scale FBSR Demonstration:**
 - Demonstrate Real Waste Tank 48 behaves like Tank 48 simulant for specific dynamic FBSR process flowsheet
- **Downstream FBSR Product Impacts**
 - Tank Farm Operations
 - Defense Waste Processing Facility Operations